Vinylphosphane—How Effective is π-Donation from Phosphorus Lone Pairs?

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Ab initio calculations show that vinylphosphane prefers a ground state geometry with the phosphorus lone pair perpendicular to the alkene π-system.

Phosphorus lone pair π-interactions seem to be largely reduced compared with those in nitrogen homologues. For example, anomeric effects involving phosphorus are effectively absent,[1] phosphorus substituted carbocations are less stabilized than iminium ion analogues,[2] and phospholes have less aromatic character than pyrroles.[3,4] Vinylphosphane (**1**) is valuable as a model compound to study the phosphorus lone pair π-interaction.[4] The recent synthesis[5] of (**1**) prompts us to communicate our theoretical investigation on this and related molecules.

If the lone pair is oriented perpendicular to the adjacent π-system, no interaction between them is possible. For vinylamine, conformation (**2b**) (with a non-planar NH_2 group) was found[2c,6] to be preferred over (**2a**) by 5.0 kcal mol^{-1} (cal = 4.184 J) (6-31G*//6-31G*), since π resonance energy is lost upon rotation of the substituent. In sharp contrast, the 'nonconjugated' geometry (**1a**) was found to be the most stable conformation of (**1**) at all levels of theory employed (Table 1).[7] At MP4/6-31G*//6-31G* including zero point energy (Z.P.E.) corrections, (**1a**) is marginally preferred (0.5 kcal mol^{-1}) over the 'conjugated' conformation (**1b**). The C_s *endo* 'nonconjugated' conformation (**1c**) is 2.6 kcal mol^{-1} (MP4/6-31G*//6-31G*) higher in energy than (**1a**).

The remarkable behaviour of (**1**) is also reflected by its geometry. Rotation of the X group in $H_2C{=}CH{-}X$ compounds out of conjugation usually lengthens the C–X bonds and shortens the length of the double bond [X = BH_2, NH_2, OH, AlH_2, PH_2 (planar), SH; 6-31G*//6-31G*]. In contrast, d(C=C) increases and $d(C{-}PH_2)$ decreases when going from the π-in-plane conformation (**1b**) to the twisted conformation (**1a**). The differences in bond lengths and energies are small, but significant (Table 2).

Since hydrogen is more electronegative than phosphorus, P–H bonds may act as electron acceptors[4] ('negative hyper-

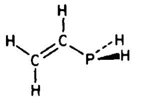
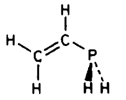
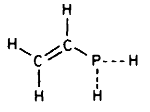
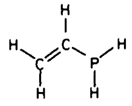
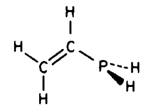
(**1a**) C_s
(**2a**) C_s

(**1b**) C_1
(**2b**) C_1

(**1c**) C_s

a; X = PH_2
b; X = NH_2

Table 1. Absolute (− atomic units) and relative (kcal mol^{-1}) energies of (**1**).

Compound	Point group	6-31G*//6-31G*	/6-31G*//6-31G* MP2	MP3	MP4SDTQ	Z.P.E. (6-31G*)	Final relative energy (MP4 + Z.P.E.)
 (**1a**)	C_s	419.32772 (0) (0.00)	419.68029 (0.00)	419.71331 (0.00)	419.73346 (0.00)	40.69	0.00
 (**1c**)	C_1	419.32586 (0) (1.17)	419.67937 (0.58)	419.71230 (0.63)	419.73259 (0.55)	40.60	0.47
 (**1b**)	C_s	419.32292 (1) (3.01)	419.67589 (2.76)	419.70897 (2.72)	419.72928 (2.62)	40.41	2.37
	C_s	419.26754 (1) (37.76)	419.62700 (33.44)	419.65931 (33.89)	419.67953 (33.84)	39.31	32.61
 Planar	C_s	419.26494 (39.39)	419.62341 (35.69)	419.65612 (35.89)	419.67608 (36.01)		

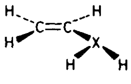
conjugation').[8] From Mulliken population analysis,[9] π-electron donation from the alkene π-system to the PH_2 group is more important in (**1a**) than in (**1b**). Hence, (**1a**) is better stabilized by the favourable alkene–PH_2 hyperconjugative interaction than (**1b**), where but one PH bond is oriented favourably with respect to the alkene. Conformation (**1b**), in addition, suffers from partial hydrogen eclipsing. These differences explain the main peculiarities of (**1**).

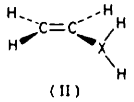
Why are the P–C π-interactions so weak in the ground state of (**1**)? Conformation (**1b**) is strongly pyramidalized at phosphorus with the lone pair oriented away from the alkene π-system. This can be probed by examining the rigid rotation with the PH_2 group held planar. Indeed, if the PH_2 group is forced to be planar, the in-plane conjugated conformation becomes *more* stable than the 90° twisted isomer (2.2 kcal mol^{-1}, MP4/6-31G*//6-31G*). The 'usual' geometry changes produced by the ligand rotation are now observed.

Rotational barriers are a measure of π-interactions in the normal configurations of the molecules, but corrections are needed for other effects (*e.g.* hydrogen eclipsing, which is *ca.* 1 kcal mol^{-1} per bond). Alternatively, we may derive estimates by subtracting the phosphorus inversion barrier in (**1**) from that of $MePH_2$, where π-resonance is absent. At centres of moderate electron demand, both measures largely agree (Table 3). This, in turn, indicates that the ground state contributions by phosphorus lone pair pπ-donation in these compounds is small.

We conclude that the lack of significant pπ-donation from phosphorus lone pairs is not due to inherently weak 1st row–2nd row orbital overlap. Planarized phosphino groups are good to excellent pπ-donors, sometimes comparable to amines. However, planarization at phosphorus is very costly compared to the gain in π-resonance energy. Lone pair pπ-donation† is usually decreased, since the phosphorus lone pair is bent away from the π system at the adjacent centre. pπ-Overlap† becomes negligible as a consequence.[12]

Table 2. Rotational barriers (kcal mol^{-1}) and variations of bond lengths [Δ*d*(C=C), Δ*d*(C–X), in Å] in $H_2C{=}CH{-}X$ upon rotation (I) → (II) of the substituent, MP2/6-31G*//6-31G*.


(I)


(II)

X	Δ*d*(C=C)	Δ*d*(C–X)	Rotational barrier
$-BH_2$	−0.0089	0.0173	7.7
$-NH_2$	−0.0064	0.0351	5.0[c]
$-OH$[a]	−0.0071	0.0372	5.6
$-AlH_2$	−0.0034	0.0162	4.2
$-PH_2$	+0.0012	−0.0012	−0.5[d]
$-PH_2$ planar[b]	−0.0012	0.0250	2.2[e]
$-SH$[a]	−0.0008	0.0195	2.0

[a] Initial conformation: dihedral angle ∢ CCOH = 0°. [b] The PH_2 group was constrained to be planar. [c] 6-31G*//6-31G*. [d] MP4/6-31G*//6-31G* including Z.P.E. [e] MP4/6-31G*//6-31G*.

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† As is generally the case,[11] population analysis shows (d–p)π interactions to be unimportant for interactions involving second row elements.

Table 3. PH_2 group inversion and rotational barriers (kcal mol^{-1}) of selected compound.

Compound	Rotation			Inversion ΔE
	Initial conformation	Twisted conformation	ΔE(rotation)	(inversion)
$H_2C=CH-PH_2$	(**1b**)	(**1a**)	-0.47^a	32.14^a
$H_2C=CH-PH_2$	planar, C_s	PH_2 planar, C_s	2.16^b	—
(Z)-$HN=CH-PH_2$	C_1	C_s	0.0^c	—
(E)-$HN=CH-PH_2$	C_1	C_s	1.4^c	—
$O=CH-PH_2$	C_1	C_s	3.44^c	23.8^c
$O=CH-PH_2$	planar, C_s	PH_2 planar, C_s	17.6^c	—
CH_3-PH_2	—	—	—	36.6^b
BH_2-PH_2	C_s	C_s	10.6^d	4.2^d
BH_2-PH_2	planar, C_{2v}	PH_2 planar, C_{2v}	40.0^d	—
AlH_2-PH_2	C_s	C_s	3.9^b	9.8^b
AlH_2-PH_2	planar, C_{2v}	PH_2 planar, C_{2v}	11.4^b	—
$H_2C-PH_2^+$	planar, C_{2v}	C_s	31.4^b	—
$H_2C-PH_2^+$	PH_2 twisted, C_s	—	—	67.5^b
$H_2C-PH_2^\cdot$	C_s	C_1	0.9^d	2.72^d
$H_2C-PH_2^{-f}$	C_s	C_1	$-9.0^{e,f}$	—

[a] MP4/6-31G*//6-31G* including Z.P.E. [b] MP4/6-31G*//6-31G*. [c] MP2/6-31G*//3-21+G. [d] MP2/6-31G*//6-31G*. [e] MP4/6-31+G*. [f] Ref. 10.

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